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SELF-DIFFUSION COEFFICIENT OF FERROMAGNETIC INTERSTITIAL SOLID SOLUTIONS

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To investigate diffusion of hydrogen in ferromagnets, the model considering the exchange interaction of the diffusing atom with "magnetic" *d*(*f*) electrons of matrix atoms was used in [1]. This allowed anomalies in the behavior of the diffusion coefficient D in the vicinity of the Curie point T_C to be explained. This model was used in [2] to describe hydrogen solubility and thermodiffusion in ferromagnetic crystals.

In the present work, this model is used to calculate the self-diffusion coefficient of diluted ferromagnetic solid solutions *A*–(*C*). It is accepted that near each interstitial atom *C*, there is one electron with uncompensated spin, so that additional interaction of exchange character of the atom *C* with site atoms *A* is observed. It disappears when the solution is converted into the paramagnetic state, that is, when the temperature exceeds T_C.

The self-diffusion coefficient for the vacancy model of diffusion hopping is determined by the following expression [3]:

$$D = \frac{a^2}{\tau_0} \cdot e^{-\frac{V}{kT}} \cdot c_\upsilon, \tag{1}$$

where a is the lattice constant, τ_0 is time of the order of the oscillation period corresponding to the maximum frequency of the acoustic spectrum of the crystal, V is the height of the potential barrier that the atom overcomes when hoping from the site to the neighboring vacancy, and c_υ is the equilibrium vacancy concentration for solution *A*–(*C*). Let us consider the crystal comprising N_A central atoms, N_C atoms incorporated into octahedral interstices, and n_υ vacancies. To characterize the magnetic ordering, we take advantage of spontaneous magnetizations μ and μ' of atoms *A* and *C* determined by the following formulas:

$$\mu = \frac{N_A^+ - \frac{N_A}{2}}{N_A}, \quad \mu' = \frac{N_C^+ - \frac{N_C}{2}}{N_C}, \tag{2}$$

where $N_\alpha^+ (\alpha = A,\ C)$ is the number of atoms α with the (+) spin, that is, oriented along the spontaneous magnetization direction. From Eq. (2) we find the probabilities of orientation of spins (+) and (–) for each atom species:

$$P_A^+ = \frac{1}{2} + \mu,\ P_A^- = \frac{1}{2} - \mu,\ P_C^+ = \frac{1}{2} + \mu',\ P_C^- = \frac{1}{2} - \mu'. \tag{3}$$

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From here we obtain the exchange energies for the *A–A* and *A–C* pairs:

$$E_{AA} = -\frac{B}{2}\left(P_A^+ - P_A^-\right)^2 = -2B\mu^2,$$
$$E_{AC} = \frac{\Im}{2}\left(P_A^+ - P_A^-\right)\left(P_C^+ - P_C^-\right) = 2\Im\mu\mu', \tag{4}$$

where B and $\Im$ are the exchange parameters; moreover, $B > 0$, $\Im$ can be both positive and negative, and the exchange interaction between atoms *C* proportional to their squared concentration is not considered.

The free energy of the system *A*–(*C*) in the approximation that considers only the interaction of the nearest neighbors is

$$F = -\frac{N_A}{1+c_\upsilon}\left\{\frac{z}{2}\upsilon_{AA} + \nu\chi c_C\upsilon_{AC} + Bz\mu^2 - 2\Im\nu\chi c_C\mu\mu'\right\}$$
$$+kTN_A(1+c_\upsilon)\{c_\upsilon\ln c_\upsilon + (1-c_\upsilon)\ln(1-c_\upsilon)\} + kT\chi N_A\{c_C\ln\frac{c_C}{1+c_\upsilon} \tag{5}$$
$$+(1+c_\upsilon-c_C)\ln\frac{1+c_\upsilon-c_C}{1+c_\upsilon}\Big\} + kTN_A\Big\{\left(\frac{1}{2}+\mu\right)\ln\left(\frac{1}{2}+\mu\right)$$
$$+\left(\frac{1}{2}-\mu\right)\ln\left(\frac{1}{2}-\mu\right) + \chi c_C\left[\left(\frac{1}{2}+\mu'\right)\ln\left(\frac{1}{2}+\mu'\right) + \left(\frac{1}{2}-\mu'\right)\ln\left(\frac{1}{2}-\mu'\right)\right]\Big\}.$$

Here υ_{AA} and υ_{AC} are the interaction energies of the nearest pairs *A–A* and *A–C* taken with the minus sign, z is the coordination number of the lattice, ν is the number of the nearest neighbors *A* for the atom *C*, χ is the ratio of the number of interstices to the number of lattice sites, $c_\upsilon = \frac{n_\upsilon}{N_A}$, and $c_C = \frac{N_C}{\chi N_A}$.

Equilibrium values of c_υ, μ, and μ' are determined from the extremum conditions for *F*:

$$\frac{\partial F}{\partial c_\upsilon} = 0, \quad \frac{\partial F}{\partial \mu} = 0, \quad \frac{\partial F}{\partial \mu'} = 0. \tag{6}$$

The first of these equations yields

$$c_\upsilon = \frac{1}{(1-c_C)^\chi}\exp\left(-\frac{u}{kT}\right), \tag{7}$$

where u is the energy of vacancy formation

$$u = \frac{z\upsilon_{AA}}{2} + c_C\nu\chi\upsilon_{AC} + 2Bz\mu^2 + 2c_C\nu\chi\Im\mu\mu'. \tag{8}$$

Because c_υ is small, μ and μ' entering into Eq. (8) must be taken at $c_\upsilon = 0$. If atoms *C* occupy octahedral interstices, $\chi = 3$ and $\nu = 2$ for BCC lattices, and $\chi = 1$ and $\nu = 6$ for the FCC lattices.

Since the vacancy concentration in solids is typically small (of the order of $10^{-4} - 10^{-3}$ at.%), we can neglect the effect of vacancies on the magnetization; in this case, the second and third equations of system (6) are written as follows:

$$-2zB\mu + 2c_C v\chi\Im\mu' + kT\ln\frac{1+2\mu}{1-2\mu} = 0,$$
$$2v\Im\mu + kT\ln\frac{1+2\mu'}{1-2\mu'} = 0. \tag{9}$$

We note that transition $c_C \to 0$ yields the equation for μ of the pure ferromagnetic crystal instead of the first equation of system (9), whereas the second equation remains unchanged. This is due to the fact that the given equation in the initial form contains the multiplier N_C on the left and on the right sides; for $c_C \neq 0$, it is reduced and yields the given equation; for $c_C = 0$ $(N_C = 0)$, it is converted into the trivial identity 0 = 0, as expected, and only the first equation remains in system (9).

System (9) at all temperatures has the solution $\mu = \mu' = 0$. The point of absolute loss of the paramagnetic state stability (the Curie temperature T_C) is determined from the equation

$$\begin{vmatrix} 1 - \dfrac{Bz}{2kT} & c_C\dfrac{v\chi\Im}{2kT} \\ \dfrac{v\Im}{2kT} & 1 \end{vmatrix} = 0, \tag{10}$$

whose solution has the form

$$T_k = T_k^{(0)} + c_C\frac{v^2\chi\Im^2}{2kzB}, \tag{11}$$

where $T_k^{(0)} = \dfrac{Bz}{2k}$ is the Curie temperature of the pure crystal *A*. According to Eq. (11), incorporation of the interstitial impurity into the crystal increases its Curie temperature for any arbitrary sign of the parameter $\Im$.

From system (9) we find

$$\mu' = -\frac{1}{2}\tanh\left(\frac{v\Im}{kT}\mu\right). \tag{12}$$

The potential barrier height *V* in Eq. (1) is equal to the difference between energies of the atom *A* at the saddle point *P* (lying in the middle of the segment connecting the atom on the lattice site with the vacancy) and at the site position with only one vacancy among its nearest neighbors. Designating by z_1 and z_2 the numbers of atoms *A* and *C* nearest to the point *P*, by v_1 the number of the nearest interstices of the site, and by B' and $\Im'$ the exchange parameters at point *P*, we obtain

$$V = -z_1\upsilon'_{AA} - z_2\chi c_C\upsilon'_{AC} - 2z_1B'\mu^2 + 2z_2\chi c_C\Im'\mu\mu'$$
$$+(z-1)\upsilon_{AA} + v_1\chi c_C\upsilon_{AC} + 2B(z-1)\mu^2 - 2v_1\chi c_C\Im\mu\mu', \tag{13}$$

where υ'_{AA} and υ'_{AC} are the energies of interaction of pairs *A*–*A* and *A*–*C* at the saddle point taken with the opposite sign.

For the BCC lattice, $z = 8$, $z_1 = 6$, $z_2 = 6$, and $v_1 = 6$; in addition, $\upsilon'_{AA} \simeq \upsilon_{AA}$ and $B' \simeq B$ (thus, the distance from point *P* to the nearest site differs only by 3% from the distance between the nearest neighbors); therefore,

$$V = \upsilon_{AA} - 18c_C\left(\upsilon'_{AC} - \upsilon_{AC}\right) + 2B\mu^2 + 36c_C\left(\Im' - \Im\right)\mu\mu'. \tag{14}$$

From this for the self-diffusion coefficient of the BCC lattice, we obtain the expression

$$D = \frac{a^2}{\left(1 - c_C\right)^3}\exp\left(-\frac{Q}{kT}\right), \tag{15}$$

where Q is the self-diffusion energy. According to Eqs. (1), (7), (8) and (14), it is

$$Q = Q_0 + \Delta Q. \tag{16}$$

Here

$$Q_0 = 5\upsilon_{AA} + 6c_C\left(4\upsilon_{AC} - 3\upsilon'_{AC}\right),\ \ \Delta Q = 14B\mu^2 + 12c_C\Im\mu\mu' + 36c_C\left(\Im' - \Im\right)\mu\mu'. \tag{17}$$

As can be seen from Eqs. (16) and (17), the activation energy bends at the Curie temperature; therefore, analogous anomaly arises in the plot $\ln D$ versus $\frac{1}{T}$, thereby causing the deviation of the temperature dependence of $\ln D$ at temperatures below T_{C} toward the $\frac{1}{T}$ axis. For the FCC lattice, $z = 12,\ z_1 = 4,\ z_2 = 2,\ \nu_1 = 6,$ and $\nu = 6$; in addition, since interstices are at the same distance from point *P* as from the site, $\upsilon'_{AC} = \upsilon_{AC}$ and $\Im' = \Im$. For *D* this yields formula (15) with $\left(1 - c_C\right)^3$ substituted by $\left(1 - c_C\right)$ and the following Q_0 and ΔQ values:

$$Q_0 = 11\upsilon_{AA} - 4\upsilon'_{AA} + 4c_C\upsilon_{AC},\ \ \Delta Q = 2\left(11B - 4B'\right)\mu^2 - 8c_C\Im\mu\mu', \tag{18}$$

thereby leading to the same anomalies of *D* in the vicinity of T_{C} as for the BCC crystal.

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